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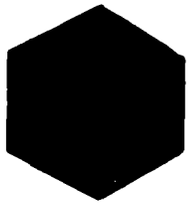

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INTERCHEMICAL CORPORATION
CENTRAL RESEARCH LABORATORIES
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RESEARCH REPORT

PROJECT NO: 94022-300

REPORT # 2 (Final)

WASHFAST INSECT REPELLENT FINISH FOR COTTON FABRICS

GOVERNMENT CONTRACT #:..DA-49-193-MD-2355.

April 15, 1963-June 30, 1963

JOHN R. ABRAMS

V. LINDSAY CHASE

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TYPE OF REPORT

Final Technical Report

PERIOD COVERED:

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PRINCIPAL INVESTIGATOR:

V. LINDSAY CHASE

INSTITUTION:

Central Research Laboratory
-of-
INTERCHEMICAL CORPORATION.

SUBJECT OF THE REPORT:

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FINISH FOR COTTON FABRICS

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ABSTRACT

1. Preparing Institution: Central Research Laboratories of Interchemical Corporation

2. Title of Report: Washfast Insect Repellent Finish for Cotton Fabrics

3. Principal Investigator: V. Lindsay Chase

4. Number of pages: 11

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Deet in various binder systems was applied to cotton fabrics by a padding operation. Because of the low order of fastness found, emphasis has shifted from repellence to mosquitos to toxicity to chiggers and samples were tested for the latter. All but one were tested only after a standardized rinse. Three gave fairly good protection from chiggers: molecular sieve-ethyl cellulose, silicone resin and vinyl copolymer. Four gave fair protection: ethyl cellulose, polyethylene, deet trapped in fiber overpadded with deet-acrylic resin and again overpadded with melamine formaldehyde resin and imine terminated polymer cured at room temperature with carboxyl containing polymer. Four gave poor protection--room temperature moisture curing polyurethane, ethyl cellulose overpadded with fluorochemical, carboxy containing acrylic terpolymer and "locked-in" deet. Contrary to results expected from previous experiments, there was one fabric in which deet could not be trapped, presumably because of a finish on the fabric. It is very difficult to determine deet content of dyed sateen. Losses by evaporation and azeotropic vaporization make direct weighing inaccurate and extractives interfere with chemical analysis. It does not appear that binders will appreciably enhance the washfastnees of deet for repellency purposes. As for toxicity to chiggers, the washfastness may be increased but probably not greatly.

Note: Copies of this report are filed with the Defense Documentation Center, Building 5, Cameron Station, Alexandria, Virginia, and may be obtained from that agency by qualified requestors.

II. DESCRIPTORS:

N,N-DIETHYLMETATOLUAMIDE
insect repellency
toxicity to insects
washfastness
binding on cotton
trapping in cotton
content of fabric
Chiggers
Mosquitos

III. INTRODUCTION:

Besides being the best practical, general purpose, individual insect repellent known, N,N-diethyltoluamide (deet) is toxic to chiggers even in minute quantities. It is however, somewhat water soluble and relatively volatile. Thus, rendering it fast to washing becomes a difficult task. It was hoped that various binders, absorbents, film formers, cross linking materials or combinations of these might significantly improve the washfastness without impairing the repellency and toxicity of deet. Thus far no system had shown promise but there were other systems to be tried and these are covered in this report.

IV. EXPERIMENTAL

Since in previous work, no promising leads were noted, emphasis has shifted from repellency to mosquitos to toxicity to chiggers. All of the samples covered in this report were tested for toxicity to chiggers.

Additional deet-binder systems evaluated are listed below. They were applied by padding, an operation in which the fabric is first passed through a bath of the composition, then through a pair of rubber squeeze rolls so that the cloth retains 50% - 70% of its weight of the liquor.

Toxicity to chiggers is determined by placing the insects on a small patch of fabric and determining how much time elapses before they die, an average of two tests being taken. Killing times of two to three minutes are excellent. Fifteen minutes or more is poor. A more practical test is also used in which the treated fabric is wrapped around the forearm and the insects allowed to crawl up to ascertain if any survive the trip to the bare arm.

As deet is slightly basic it was applied with an acrylic polymer latex containing acid groups in the polymer (Formula A) to determine if it would be held strongly enough to increase its washfastness without impairing its repellency.

FORMULA A

Acrysol ASE 60 (28% solids)	38.8%
Water	40.8%
Deet emulsion (49% deet; 1.65% Span 20; 0.35% Tween 20)	20.4%
	100.0%

The repellency of the deet was lost after a rinsing one hour in fifty times the cloth weight of cold water.

As polyethylene from emulsions adheres well, although not a film former and should absorb deet, it was blended with deet (Formula B) and applied to olive sateen. After rinsing this gave fair protection against chiggers (6 min. 40 sec. to kill).

FORMULA B

Spencer Polyethylene Emulsion (non-ionic) 40%	50.0%
Deet Emulsion (Deet-50%; Span 60-1%; Tween 60-1%)	20.0%
Water	30.0%
	100.0%

Vinyl resins are very retentive of plasticizer, so deet was used to replace part of the plasticizer in a vinyl plastisol system. Deet, however, is such a powerful solvent for vinyl resin that the system gelled just after the vinyl resin was stirred in. When the system included considerable mineral spirits gelation was prevented, but upon application to the fabric the mineral spirits, deet and dioctyl phthalate wicked away from the vinyl resin, which then sat up on the surface of the fabric implasticized. The system then was changed to a vinyl solution system. (Formula C) This gave fairly good protection against chiggers (4 min. 50 sec. to kill)

FORMULA C

Vinylite VYNS	20.0%
Dioctyl Phthalate	5.0%
Deet	10.0%
Tetrohydrofurfural	65.0%
	100.0%

Deet was "trapped" in the fabric (Formula D) by air drying and heating, a deet-binder film (Acryloid AT-50, Formula E) was applied and allowed to dry, then a binder (Formula F) without deet, incompatible with the Acryloid AT-50 and in a different solvent was applied. After drying the whole system was cured 3 minutes at 300° F. during which time considerable deet volatilized. After the usual rinse this gave fair protection against chiggers (6 min. 20 sec. to kill).

FORMULA D

Water	58.8% (Vol.)
Denatured Alchohol	32.4
Deet	8.8
	100.0%

FORMULA E

Acryloid AT-50 (50%)	20. gm.
Deet	10. gm.
Toluene	60. gm.
	90. gm.
	(about 100 ml.)

FORMULA F

Resloom M-80 (80%)	20.0%
Water	79.7%
Ammonium nitrate	.3%
	100.0%

As the curing operation drives off considerable deet, room temperature curing systems were tried. An imine terminated polymer and a carboxyl containing acrylic terpolymer as reactants in an emulsion system (Formula G) and a moisture (from the air) cured polyurethane solution (Formula H) were the compositions tested. These blended with deet were applied to fabric and allowed to dry and cure at room conditions. After rinsing the former provided fair protection (6 min. 5 sec. to kill) and the latter poor protection (15 + min.) against chiggers.

FORMULA G

1.	Carboxyl containing acrylic terpolymer	18.0%
2.	Imine terminated polymer	3.0%
3.	Deet	10.0%
4.	Water	69.0%
		100.0%

2 diluted with 3 and emulsified into 1 diluted with part of 4. Rest of 4 added.

FORMULA H

Chemiglaze EX B751 - 6A	43. gm.
Deet	10. gm.
Toluene	41. gm.
	94. gm.
	(about 100 ml.)

It was thought that a silicone resin (a flexible insulating varnish) as a binder for deet might be less permeable to wash liquor and thus enhance washfastness. SR 224 Silicone Resin (General Electric Co.) and deet (Formula I) were applied to olive sateen, cured 4 minutes at 90° - 100° C. and 4 minutes at 150° C. and rinsed. This fabric gave fairly good protection (4 min. 32 sec. to kill) against chiggers.

FORMULA I

SR 224 Silicone Resin 60%	28.0%
Deet	10.0%
Toluene	62.0%
	100.0%

It was hoped that if deet were absorbed in a molecular sieve (dihydrated zeolite) and the latter held on fabric with a binder the deet might be released gradually. If water gets through the binder, however, it would probably replace the deet as it replaces any other material in a molecular sieve. Deet absorbed in molecular sieve 13X was bound on fabric by ethyl cellulose (Formula J). The composition was rinsed after air drying and gave fairly good protection (4 min. 35 sec. to kill) against chiggers.

FORMULA J

1.	Molecular Sieve 13x powder (Linde Company)	25.0%
2.	Deet	10.0%
3.	Aroplaz 1273	3.3%
4.	Toluene	55.0%
5.	Ethyl Cellulose N 4 (Hercules Powder Company)	6.7%
		100.0%

1, 2 tumbled with uniform. 3, 4 premixed and 5 dissolved therein. 1, 2 dispersed in 3, 4, 5.

If a fluorochemical in non-aqueous solution were applied over binder-deet film, the water repellency might be sufficiently increased to improve the washfastness. Since deet is effective when bound by ethyl cellulose, this combination (Formula K) was applied to the sateen and overpadded with a 1% solution of Fluorochemical FX-310 (Minn. Mining and Mfg. Co.) in carbon tetrachloride. After the standard rinse this gave poor protection (15 + min. to kill) against chiggers. Deet ethyl cellulose on white twill gave fairly good protection before (4 min. 30 sec. to kill), and fair protection after rinsing (6 min. 30 sec. to kill) against chiggers. Perhaps the fluorochemical seals in the deet blocking its action.

FORMULA K

Ethyl Cellulose N-4 (Hercules Powder Company)	10.0%
Deet	10.0%
Denatured alcohol	16.0%
Toluene	64.0%
	100.0%

The U.S. Department of Agriculture's Entomology Research Division Laboratory at Gainesville, Florida submitted some white twill fabric in which deet was to be "trapped" or "locked". When applied from water alcohol solution (Formula L), allowed to dry and heated at 300°F. for fifteen minutes only 0.2% instead of the usual 3.5% - 4.0% was trapped in the fabric. After repeating the operation and obtaining the same result an emulsion system (Formula M) was used, again with the same result. To check the system a piece of 80 x 80 cotton print cloth was treated with the emulsion, air dried and heated 15 minutes at 300°F. It retained 4.4% deet. Apparently a finish on the twill is interfering with either the absorption or retention of deet. The treated print cloth was submitted and found to give poor (15 + min. to kill) protection against chiggers. "Locked in" deet had previously been found not to repel mosquitos. It seemed that although there was sufficient deet present for repellency and toxicity, more than usual atmospheric moisture is needed to bring the deet to the surface of the fiber.

FORMULA L

Deet	10.0% vol.
Denatured alcohol	32.0% vol.
Water	58.0% vol.
	100.0% vol.

FORMULA M

Water	15.00%
Tween 60	.31%
Deet	15.00%
Span 60	.31%
Water	69.38%
	100.00%

Tween 60 dissolved in 15 parts of water using heat. Span 60 dissolved in deet and emulsified into the Tween 60 - water mixture by high speed mixing. Rest of water added during stiring.

All of the fabrics having a binder thereon are at least slightly stiffened. Whether this stiffness would make the sateen unacceptable to the Army is not known.

Although the ultimate criterion is the repellency and toxicity of the fabric it is desirable to know the deet content of the fabric expecially after rinsing. Determination of the amount of deet on fabric presents several problems. If the fabric could be brought to bone dry condition before and after, the amount of deet could be found. Drying the cloth, however, requires considerable heat which vaporizes much of the deet. Use of a dessicator did not prove satisfactory, probably because air circulation is so slow and amount of cloth so large that very long times were required. Pre-and post-conditioning in a temperature and humidity controlled room also was found unsatisfactory probably because the control was not sufficiently precise.

Extreme difficulties have been encountered in quantitative analysis for deet. Extraction with a solvent (chloroform) also leaches out black Tarry material which is probably a mixture of dye, lubricant and size.

The best procedure seemed to be to obtain wet pickup of the formulation by the fabric and calculate the deet content of the dried fabric by running solids content of the formulation on a thin film at room temperature. Two drops of the mixture were placed on a 1" x 3" microscope slide, covered with another slide to spread the mixture, the slides separated and allowed to dry at room temperature for two hours. The weight of the wet mixture was obtained by difference from a dropper bottle.

Under these conditions about 10% of the deet is lost mostly by azeotropic vaporization but partly by evaporation which continues after the water has evaporated. It does appear, however, that losses of deet from fabric are higher than from glass.

The U. S. Department of Agriculture Entomological Research Division Laboratory at Gainesville, Florida will run more tests on the samples after additional rinsing and washing. When these results are obtained a supplementary note to this report will be issued.

V. SUMMARY:

Various compositions were applied to sateen and given a rinse treatment. Several gave good protection against chiggers. These were:

Deet on molecular sieve bound by ethyl cellulose.
Deet-silicone resin
Deet-vinyl copolymer

Those listed below gave fair protection against chiggers.

Deet-ethyl cellulose
Deet-polyethylene (emulsion)
Deet trapped in fiber overpadded with deet acrylic binder which in turn was overpadded with aqueous melamine formaldehyde resin (not compatible with the acrylic resin).
Deet-room temperature curing binder (imine terminated polymer cured with carboxyl containing acrylic terpolymer)

The following gave poor, if any protection:

Deet
Room temperature, moisture curing polyurethane binder.
Deet-ethyl cellulose overpadded with fluorochemical.
Deet-carboxy-containing acrylic polymer.
Locked in deet.

These samples were not tested for repellency although stockings were impregnated for the test, if chigger results indicated promise.

Because of volatility of deet alone or as an azeotrope and because of contaminants in extracting deet from fabrics for analysis it has been difficult to make a direct measurement of the amount of deet in treated fabric. Approximations can be made if the wet pick up of the treating liquor is determined and the deet content of the liquor measured by drying the liquor in thin films on glass.

VI. CONSOLIDATED SUMMARY: (From Interim Report)

A summary of the work covered in the interim report follows.

A satisfactory emulsion system for deet was developed.

Deet was found to be water soluble to the extent of 1.2% at room temperature.

The following binder systems were applied to sateen and stockings (cotton) and tested for washfastness and repellency.

Acrylic terpolymer latex
Melamine-formaldehyde resin
Thermosetting acrylic binder-thickener-latex combination
Ethyl cellulose - solvent system
Acrylic latex - calcium silicate adsorbent-water system
Ethyl cellulose - calcium silicate-solvent system

On the basis of mosquito repellency tests none were washfast and the acrylic latex - calcium silicate - adsorbent aqueous system was not repellent before washing.

If water were present during application, deet was trapped in the fiber after drying with subsequent heating at 300° F. for 15 minutes. This "locked-in" deet, however, did not impart repellency and could still be readily washed out with water.

VII. CONCLUSIONS:

Since deet is appreciably soluble in water, fixing it on fabric so as to be washfast becomes a very difficult task. In addition deet is appreciably volatile which pretty much limits binder systems to room or very low temperature cures.

Since in a couple of cases bound deet was not repellent even before washing yet readily rinsed out of the fabric it does not appear that deet can be bound on to resist washing and still be repellent.

Since toxicity to chiggers requires a much smaller quantity of deet and since various samples show rather good protection against chiggers after a single prolonged rinse, it appears that some binder system might still retain satisfactory protection against chiggers after limited washing.

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